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(54) Title: PROCESS FOR THE PREPARATION OF A CATALYST

(57) Abstract

The present invention relates to a process for the preparation of a catalyst of the Ziegler Natta type. According to this process a solid component, comprising basically atoms of halogen, magnesium and a transition metal of groups IV, V or VI of the Periodic Classification of the Elements, is contacted with an electron donor compound. The solid component is advantageously prepared by a reaction between metallic magnesium, a monohalogenated hydrocarbon and at least one compound of a transition metal.

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PROCESS FOR THE PREPARATION OF A CATALYST

The present invention relates to a process for the preparation of a catalyst of the Ziegler-Natta type. It also relates to an olefin polymerisation process using the prepared catalyst.

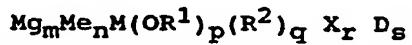
According to French Patents no 2 116 698 and no 2 099 311 it is known to prepare a catalyst of the Ziegler-Natta type which can be employed for the polymerisation of olefins and especially for the polymerisation of ethylene. According to French Patent no 2 116 698 it is prepared by the reaction of magnesium in the metallic state with a monohalogenated hydrocarbon, an ether and a derivative of a transition metal in a valency state of at least 4. According to French Patent no 2 099 311 a catalyst is prepared by the reaction of activated magnesium, with a monohalogenated hydrocarbon and a derivative of a transition metal in a valency state of at least 4.

Such catalysts are effective but have a catalytic activity which increases rapidly with increasing polymerisation temperature, especially in the temperature range generally employed for olefin polymerisation reactions. As a result, when such catalysts are used, it is generally found that a small change in the reaction temperature can entail a relatively large change in the activity of the catalyst and consequently in the rate of polymerisation. This phenomenon is particularly troublesome when starting a polymerisation reaction, where temperature changes can occur in an unpredictable manner. A change in the rate of polymerisation can promote the formation of polymer agglomerates, especially in a gas phase polymerisation process, for example in a fluidised bed.

The present invention relates to the preparation of a polymerisation catalyst which overcomes or at least mitigates the problems associated with these known catalysts. The catalyst prepared according to the present invention has a relatively stable activity over the desired range of temperature, that is to say a slight change in the temperature does not result in a large change in the catalyst activity. This ensures that the catalyst is better adapted to use in a large scale commercial reactor.

The subject of the present invention is therefore a process for the preparation of a catalyst of the Ziegler-Natta type characterised in that it comprises contacting a solid component comprising atoms of halogen, magnesium and a transition metal of groups IV, V or VI of the Periodic Classification of the Elements, with an electron donor compound.

The solid component used according to the invention preferably corresponds to the general formula:



in which Me is an atom of aluminium and/or zinc, M is an atom of a transition metal belonging to groups IV, V, or VI of the Periodic Classification of the Elements, preferably an atom of titanium and/or vanadium, R<sup>1</sup> is an alkyl group comprising from 1 to 14 carbon atoms, R<sup>2</sup> is an alkyl group comprising from 1 to 12 carbon atoms, X is an atom of chlorine and/or bromine, D is an electron donor compound comprising preferably atoms of oxygen, sulphur, nitrogen, or phosphorus, and where,

m is from 1.5 to 50, preferably from 2 to 10,  
n is from 0 to 2, preferably from 0 to 1,  
p is from 0 to 4, preferably from 0 to 3,  
q is from 0 to 1, preferably from 0 to 0.5,  
r is from 4 to 110, preferably from 5 to 27, and  
s is from 0 to 0.5, preferably from 0 to 0.2.

The invention is particularly suitable for use with a solid component prepared by a reaction between magnesium in the metallic state, at least one monohalogenated hydrocarbon and at least one compound of a transition metal of groups IV, V or VI of the Periodic

Classification of the Elements, taken in a valency state of at least 4, optionally in the presence of an electron donor compound. The solid component can be prepared without magnesium derivative compounds. The solid component can advantageously be prepared as 5 described in French Patent no 2 099 311 or n° 2 116 698. Generally, the solid component prepared according to these patents consists of particles which have an irregular shape.

For the preparation of the solid component, the transition metal of groups IV, V, or VI of the Periodic Classification of the 10 Elements is preferably titanium and/or vanadium. Titanium compounds employed are advantageously the tetravalent compounds of titanium of formula  $TiX_{4-t} (OR^3)_t$  in which X denotes a halogen atom, generally chlorine or bromine,  $R^3$  an alkyl radical which can contain from 2 to 8 carbon atoms and t a whole or fractional number which can take any 15 value from 0 to 4, for example from 0 to 3 and preferably equal to or close to 2. Typically, titanium compounds corresponding to this definition are titanium tetrachloride, alkyl tetratitanates of formula  $Ti(OR^3)_4$  in which  $R^3$  is a radical corresponding to the above formula, or a mixture of titanium tetrachloride and of an alkyl 20 tetratitanate.

The magnesium used in the preparation of the solid component is preferably solid metallic magnesium. Typically, the magnesium is used in the form of powder or turnings. The magnesium preferably comprises magnesium of high purity. In order to avoid a long induction period 25 the magnesium is preferably reacted in an active form, that is to say in a form which is substantially free from impurities e.g. due to oxidation of the metal. Preliminary activation of the magnesium can be effected, for example, by grinding the metal in an inert atmosphere or within an inert liquid such as an aliphatic solvent. 30 Preferably, the activation can be effected by treating the magnesium with iodine vapor. It is more convenient, however to activate the magnesium in the reaction medium, for example, by introducing into the medium, small amounts of substances such as iodine, alcoholates of metals of groups IA, IIIA or IIIB of the Periodic Classification of 35 the Elements, alkyl titanate, etheroxides or alcohols such as

isobutanol. For example, a substance can represent by weight less than 10 % and preferably less than 5 % of the quantity of magnesium used.

5 The monohalogenated hydrocarbon compound is preferably selected from chlorinated or brominated derivatives of saturated aliphatic hydrocarbons. It can have the general formula  $R^4-Z$  in which Z is bromine or chlorine and  $R^4$  is an alkyl group having from 1 to 10 carbon atoms. Typically, the monohalogenated hydrocarbon is ethyl chloride, propyl chloride, butyl chloride, pentyl chloride.

10 The reaction for preparing the solid component can be effected using different modes of operation. Thus, for example, the different reactants can be introduced into an inert solvent at a temperature which is sufficiently low for the reaction not to be initiated. The reaction mixture, if necessary after the addition of a magnesium 15 activating agent such as iodine crystals, is then heated with agitation, at a temperature which is generally from -20 to 150°C, preferably from 40 to 100°C, for a period of a few minutes to 30 hours. During the reaction no milling operation is needed.

At the end of the preparation, the solid component is 20 advantageously washed with a liquid hydrocarbon, at a temperature from 10 to 50°C and preferably at a temperature close to 20°C. It is preferred not to heat the solid product obtained to a temperature higher than 100°C, and preferably not higher than 90°C.

25 In order to obtain an active catalyst it is preferred to prepare the solid component by reacting amounts of reactants such that, the molar ratio between the monohalogenated hydrocarbon and the magnesium is between 0.5 and 10 preferably between 1 and 4, the molar ratio between the transition metal and the magnesium is less than 1 and preferably less than 0.5.

30 The process of the invention comprises contacting the solid component with an electron donor compound. The latter is an organic compound. Preferably, it is free from labile hydrogen atom. It can be chosen, for example, from amongst aliphatic ethers, tertiary phosphines, tertiary amines, secondary amides and organosilicon 35 compounds. Advantageously, dimethylformamide or hexamethylphosphoro-

triamide is employed. It is generally employed in a quantity such that the molar ratio of the quantity of electron donor compound to the quantity of transition metal present in the solid component is between 0.01 and 0.1 and in particular between 0.02 and 0.07.

5       The contact operation between the solid component and the electron donor compound is generally brought about in a liquid hydrocarbon which is kept stirred and under conditions such that a maximum quantity of electron donor compound becomes bound to the solid. The liquid hydrocarbon can be an alkane or a cycloalkane which  
10      has, for example, from 4 to 10 carbon atoms, or an aromatic hydrocarbon which has, for example, from 6 to 14 carbon atoms. This contact operation is in most cases brought about at a temperature ranging from 20 to 100°C, preferably from 40 to 90°C. The operation can be carried out in various ways, for example by adding the  
15      electron donor compound to the solid component in suspension in the liquid hydrocarbon. This addition is preferably performed slowly so as to bind the electron donor compound homogeneously. It can last, for example, between 10 and 600 minutes and in most cases between 15 and 30 minutes. Following this addition, the stirring of the obtained  
20      suspension can last from 30 minutes to 5 hours. This contact operation is generally brought about in the absence of any cocatalysts such as organoaluminium compounds and in the absence of any olefins.

At the end of the contact operation the quantity of electron  
25      donor compound remaining in the free state in the liquid hydrocarbon can be nil or relatively small. It is preferable, however, to wash the solid product resulting from this contact in order to remove all the impurities present in the liquid hydrocarbon.

Using the process of the invention a solid catalyst is obtained  
30      which has a catalytic activity substantially constant over a useful range. This range is generally from 85 to 95°C.

The catalyst prepared according to the process of the present invention is used in the presence of a cocatalyst in a process for the polymerisation of olefins containing from 2 to 8 carbon atoms.  
35      The catalyst is advantageously used for the polymerisation of

ethylene optionally mixed with an alpha-olefin such as 1-butene, with a view to the manufacture of a high density, a linear low density or a very low density polyethylene. This polyethylene has a density which can range from 0.890 to 0.965. The polymerisation temperature 5 is preferably chosen in the temperature range where the catalyst activity has stabilised. The polymerisation temperature is generally from 70 to 100°C, preferably from 70 to 90°C for preparing linear low density polyethylenes, and preferably from 85 to 95°C for preparing high density polyethylenes.

10 The olefin polymerisation can be performed within a liquid in which the catalyst is dispersed and which can be an olefin in the liquid state or a saturated aliphatic hydrocarbon.

15 The polymerisation can also be performed in the gaseous phase according to known techniques in a gas phase polymerisation reactor which may be a reactor with a fluidised and/or mechanically stirred bed like those described in French Patent n° 2 207 145 or French Patent no 2 335 526. For gas phase polymerisations the catalyst is advantageously used in the form of a prepolymer prepared beforehand by bringing the catalyst into contact with ethylene optionally mixed 20 with one or more olefins, the contact being brought about in the presence of a cocatalyst and optionally in the presence of hydrogen.

25 Surprisingly, it is found that a prepolymer obtained with the catalyst of the invention contains a relatively small quantity of fine particles. This quantity is, in particular, smaller than that obtained under identical prepolymerisation conditions with a catalyst prepared without contact with an electron donor compound.

30 The cocatalyst is chosen from the organometallic compounds of metals of groups II or III of the Periodic Classification of the elements, such as organoaluminium, organomagnesium or organozinc compounds. Typically, the cocatalyst is a trialkylaluminium. The cocatalyst can be introduced into the polymerisation reactor within a prepolymer or separately.

The following examples illustrate the present invention.

35 Figure 1 shows diagrammatically a fluidised bed reactor consisting essentially of a vertical cylinder surmounted by a

disengagement chamber which is used in Examples 1 and 2.

Figure 2 shows curves of the catalytic activity of two different catalysts as a function of the temperature : the lower curve corresponds to a catalyst according to the invention and the upper curve to a comparative catalyst.

Figure 1 shows diagrammatically a fluidised bed reactor consisting essentially of a vertical cylinder (2) surmounted by a disengagement chamber (3), provided in its lower part with a fluidisation grid (4) and with a recycle conduit (5) connecting the top of the disengagement chamber to the lower part of the reactor which is situated under the fluidisation grid, which is equipped with a heat exchanger (6) a compressor (7) and feed conduits for ethylene (8) comonomer e.g. 1-butene (9) and chain transfer agent e.g. hydrogen (10). The reactor is also equipped with a feed conduit for catalyst (11) and a conduit for drawing off polymer (12).

#### Example 1

##### a) Preparation of a catalyst

4.6 m<sup>3</sup> of n-hexane, 5.5 kg of iodine, 3160 moles of magnesium, 29 moles of isobutanol, 60 moles of n-propyl titanate and 60 moles of n-butyl chloride were introduced into a reactor 10 m<sup>3</sup> in volume provided with a mechanical stirring system rotating at 100 revolutions per minute. The reactor was then heated to a temperature of 85°C until the reaction began and then the temperature was maintained to 80°C. At this temperature 340 moles of n-propyl titanate, 400 moles of titanium tetrachloride, and then 4700 moles of n-butyl chloride were introduced into the reactor over 240 minutes. The mixture thus obtained was then kept stirred at 80°C for 2 hours. At the end of this time 44 moles of an electron donor, dimethylformamide were introduced into the reactor in 20 minutes. Stirring was continued for a further 60 minutes. The reactor was cooled to room temperature and the n-hexane containing the unreacted n-butyl chloride was replaced with pure n-hexane. Thus the catalyst was obtained as a suspension in n-hexane.

##### b) Preparation of a prepolymer

500 litres of n-hexane, 2 moles of tri-n-octylaluminium and a

quantity of the catalyst prepared previously, containing 2.5 moles of titanium, were introduced into a 1.5 m<sup>3</sup> stainless steel reactor maintained under a nitrogen atmosphere. The reactor had a stirring device which was rotated at 150 revolutions per minute and was heated to 70°C. Hydrogen was then introduced into the reactor so as to obtain a partial pressure of 1 kPa, and ethylene was introduced at a steady flow rate of 15 kg/h for 6 hours 40 minutes. At the end of this time the reactor was degassed and its content was transferred to a mechanically stirred evaporator in which the n-hexane was removed by circulating nitrogen heated to 70°C. 100 kg of a prepolymer were thus obtained, ready for use, containing 40 g of polyethylene per millimole of titanium.

c) Manufacture of a high density polyethylene

The operation was carried out in a gas phase polymerisation reactor substantially as shown diagrammatically in Figure 1 having a vertical cylinder (2) 90 cm in diameter and 6 m high.

The reactor contained a fluidised bed of particles of ethylene polymer being formed. The bed had a height of 2 m and was traversed by an upward stream of a reaction gas mixture. The gas mixture had an upward velocity of 50 cm/s. The total pressure was 1.7 MPa and the temperature measured at the exit of the disengagement chamber was 90°C.

The reaction gas mixture comprised, by volume, 30 % of ethylene, 1.6 % of 1-butene, 21 % of hydrogen and 47.4 % of nitrogen. The reactor was fed with the prepolymer prepared previously at a rate of 600 g/hour. It was also separately fed with triethylaluminium in a quantity such that the molar ratio of the added aluminium to the titanium of the prepolymer was 1.2.

Under these conditions a polyethylene was drawn off at a rate of 70 kg/hour. The polyethylene had a relative density of 0.960, a titanium content of 10 ppm and contained approximately 1 % by weight of 1-butene.

Example 2

a) Preparation of a solid component

The solid component was prepared as for the catalyst in Example

1 (a) except that no dimethylformamide was used.

b) Preparation of a prepolymer

500 litres of n-hexane, 0.125 mole of dimethylformamide and a quantity of the solid component prepared previously, containing

5 2.5 moles of titanium was introduced into a 1.5-m<sup>3</sup> stainless steel reactor maintained under a nitrogen atmosphere, provided with a stirring device rotating at 150 revolutions per minute and heated to 50°C. The mixture obtained was stirred for 30 minutes at 50°C to obtain a catalyst suspension and then 2 moles of tri-n-octylaluminium  
10 was introduced into the reactor. The mixture obtained was stirred during 30 minutes at 50°C. Hydrogen was then introduced into it so as to obtain a partial pressure of 1 kPa, and ethylene was introduced at a steady flow rate of 15 kg/h for 6 hours 40 minutes. During the polymerisation reaction the reactor was maintained at 70°C. At the  
15 end of the reaction the reactor was degassed and its content was transferred to a mechanically stirred evaporator in which the n-hexane was removed by circulating nitrogen heated to 70°C. 100 kg of a prepolymer were thus obtained, ready for use, containing 40 g of polyethylene per millimole of titanium.

20 c) Manufacture of a linear low density polyethylene

The process was carried out in the same gas phase reactor as described in Example 1. (c).

25 The reactor contained a fluidised bed of particles of ethylene polymer being formed. The bed had a height of 2 m and was traversed by an upward stream of a reaction gas mixture. The reaction gas mixture had an upward velocity of 50 cm/s. The total pressure was 1.7 MPa and the temperature measured at the exit of the disengagement section was 80°C.

30 The reaction gas mixture comprised, by volume, 30 % of ethylene, 13.5 % of 1-butene, 6 % of hydrogen and 50.5 % of nitrogen.

The reactor was fed with the prepolymer prepared previously at a rate of 600 g/hour. It was also separately fed with triethylaluminium in a quantity such that the molar ratio of the added aluminium and the titanium of the prepolymer was 1.2.

35 Under these conditions a polyethylene is drawn off at a rate of

70 kg/hour which had a relative density of 0.918, a titanium content of 10 ppm and which contained approximately 8 % by weight of 1-butene.

**Example 3**

**5 Measurement of the catalyst activity**

Two series of gas-phase ethylene polymerisation reactions were carried out in a 2.5-litre stainless steel reactor provided with a stirring system rotating at 300 revolutions per minute and with a temperature control system. The first series was performed with the aid of a prepolymer prepared with the catalyst of Example 1, in which the molar ratio of aluminium to titanium is 1.5 and which contained 40 g of polyethylene per millimole of titanium. The second series was performed with the aid of a prepolymer prepared with a comparative catalyst prepared as in Example 1 except for the fact that no dimethylformamide was employed, and in which the molar ratio of aluminium to titanium was 1.2 and which contained 40 g of polyethylene per millimole of titanium.

In each series a number of polymerisation reactions were carried out at different temperatures. In each reaction there were introduced into the reactor 200 g of polyethylene as charge powder, a quantity of prepolymer containing 0.5 millimole of titanium, a quantity of hydrogen such as to have a partial pressure of 0.1 MPa and ethylene so as to maintain a total pressure of 0.4 MPa. The activity of the catalyst was measured in the case of each reaction, that is to say the quantity of polyethylene produced in grams per millimole of titanium present in the reactor and per hour of reaction.

These measurements enabled the curve of the catalyst activity to be plotted for each catalyst as a function of the temperature (Figure 2). The lower curve corresponds to the catalyst according to the invention, while the upper curve corresponded to the comparative catalyst. The lower curve showed that the activity of the catalyst according to the invention had practically stabilised above 85°C, while the activity of the comparative catalyst still continued to increase.

Claims:

1. A process for the preparation of a Ziegler-Natta type catalyst characterised in that it comprises contacting a solid component comprising atoms of halogen, magnesium and a transition metal of groups IV, V or VI of the Periodic Classification of the Elements,  
5 with an electron donor compound.
2. A process according to Claim 1, characterised in that the solid component is prepared by a reaction between magnesium in the metallic state, at least one monohalogenated hydrocarbon and at least one compound of a transition metal of groups IV, V, and VI of the  
10 Periodic Classification of the Elements, the transition metal having a valency state of at least 4.
3. A process according to Claim 1 or to Claim 2, characterised in that the electron donor compound is employed in a quantity such that the molar ratio of the quantity of electron donor compound to the  
15 quantity of transition metal present in the solid component is from 0.01 to 0.1.
4. A process according to any one of Claims 1 to 3, characterised in that the electron donor compound is a compound free from labile hydrogen.  
20 5. A process according to Claim 4, characterised in that the electron donor compound is dimethylformamide or hexamethylphosphorotriamide.
6. A catalyst obtainable by the process according to any one of Claims 1 to 5.
- 25 7. A prepolymer prepared by using the catalyst according to Claim

6.

8. An olefin polymerisation process characterised in that it uses a catalyst according to Claim 6 or a prepolymer according to Claim 7.

9. A process according to Claim 8, characterised in that the  
5 polymerisation is performed in the gaseous phase.

10. A process according to Claim 8 or to Claim 9, characterised in that the temperature of the polymerisation is from 85 to 95°C.

11. A polymer obtainable by the process according to any one of Claims 8 to 10.

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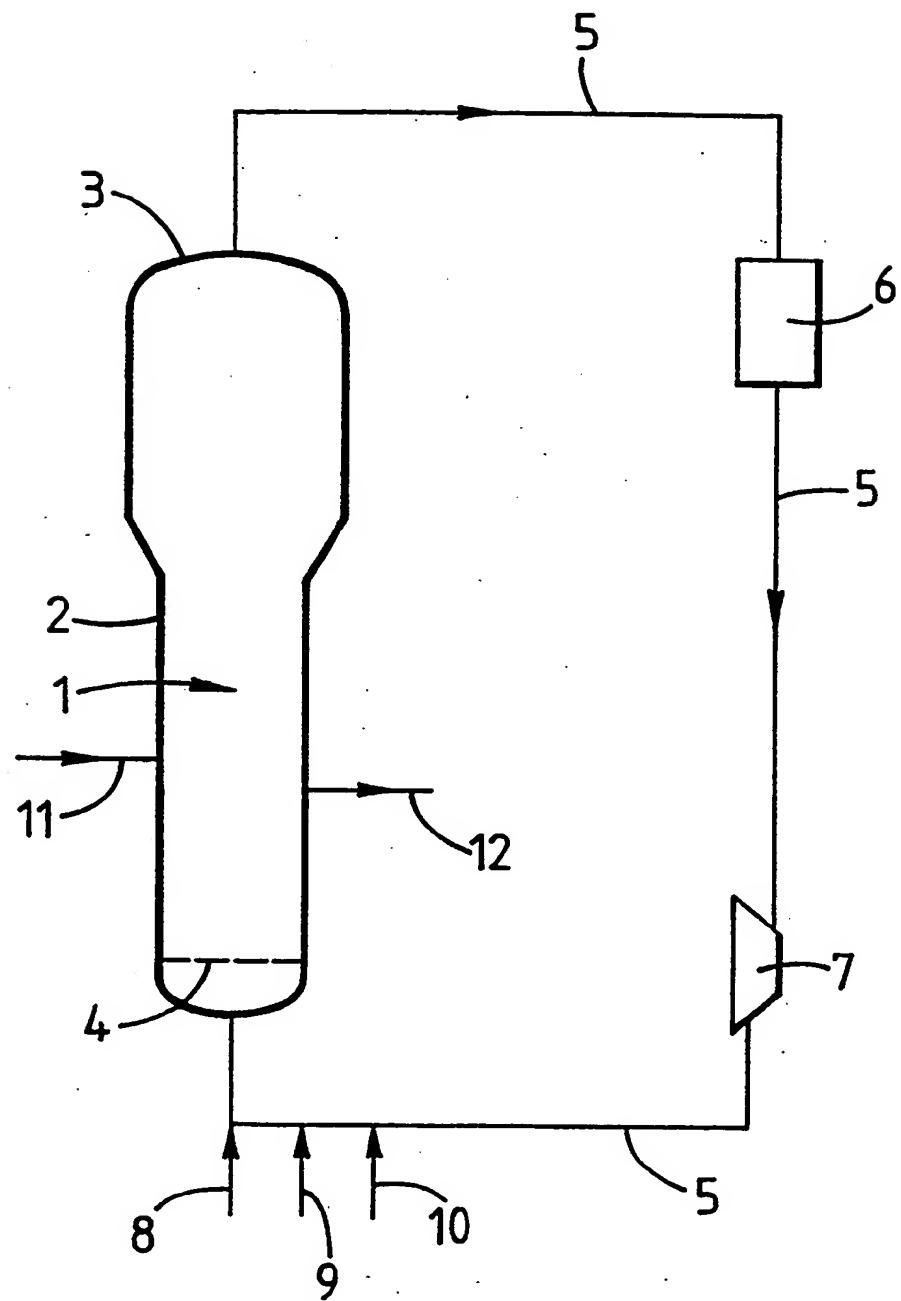
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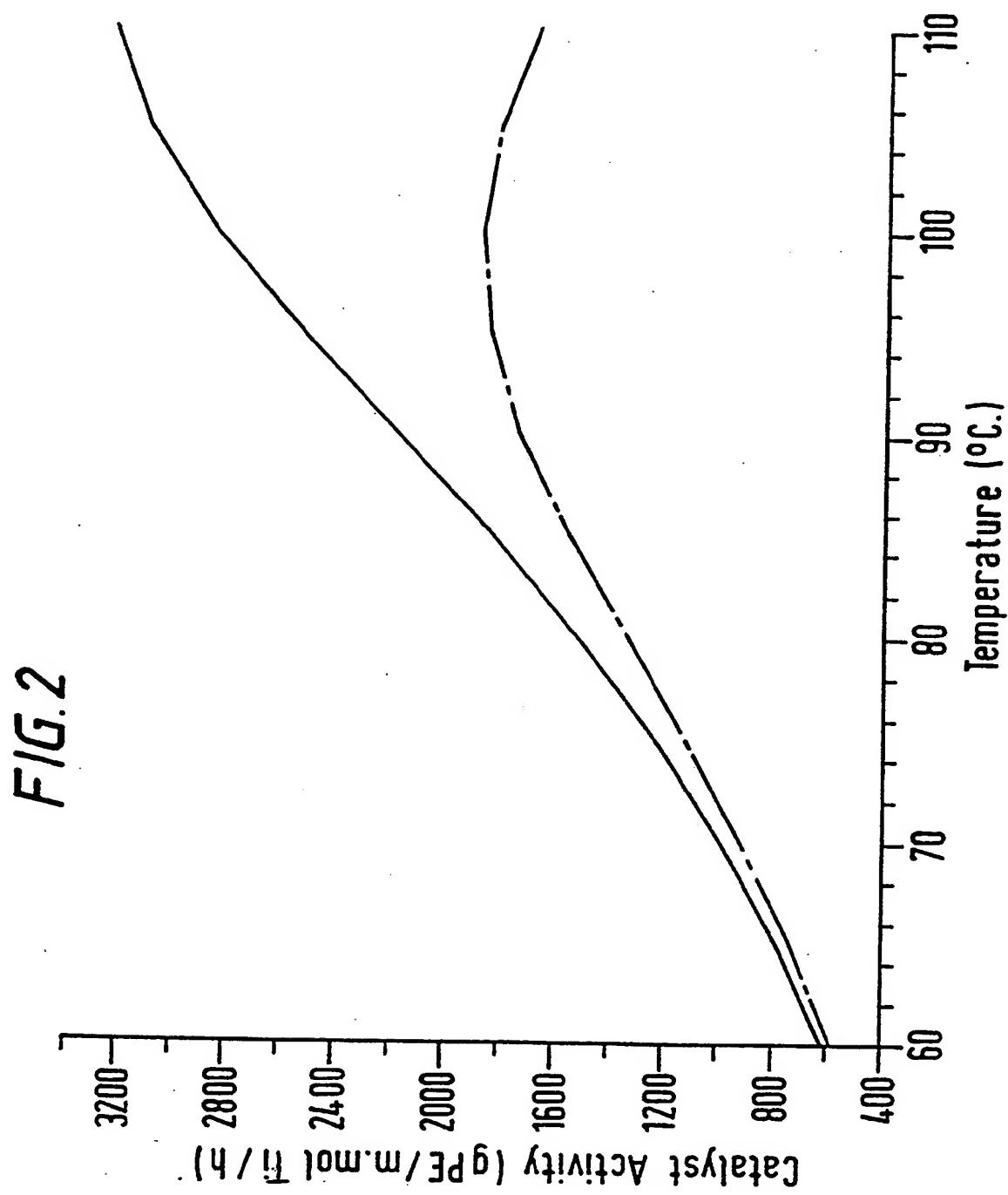
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FIG. 1





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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 93/01166

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C08F10/02; C08F4/42; C08F2/34

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

| Classification System | Classification Symbols |
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| Int.C1. 5             | C08F                   |

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

| Category <sup>10</sup> | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>   | Relevant to Claim No. <sup>13</sup> |
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| X                      | GB,A,2 103 226 (AGIP PETROLI SPA)<br>16 February 1983<br>see claims 1,3,7<br>see examples 3,6<br>see page 2, line 32 - line 36<br>----   | 1-3,8,10                            |
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## IV. CERTIFICATION

Date of the Actual Completion of the International Search

26 AUGUST 1993

Date of Mailing of this International Search Report

10.09.93

International Searching Authority

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Signature of Authorized Officer

FISCHER B.R.

| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> (CONTINUED FROM THE SECOND SHEET) |   |                              |
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9301166  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 26/08/93

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|  |                  | SE-A-                   | 8204474  | 27-07-82         |
|  |                  | SU-A-                   | 1688788  | 30-10-91         |
|  |                  | US-A-                   | 4446289  | 01-05-84         |
| -----                                  | -----            | -----                   | -----    | -----            |
| EP-A-0452156                           | 16-10-91         | JP-A-                   | 3294304  | 25-12-91         |
|  |                  | CN-A-                   | 1057656  | 08-01-92         |
|  |                  | JP-A-                   | 4218508  | 10-08-92         |
|  |                  | JP-A-                   | 4218509  | 10-08-92         |
|  |                  | JP-A-                   | 4218510  | 10-08-92         |
| -----                                  | -----            | -----                   | -----    | -----            |

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